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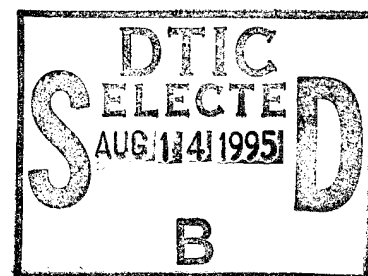
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**X-Ray StandingWave Studies of Adsorption Geometries at Selected Metal
III-V Semiconductor Surfaces**

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Introduction

The research under the ONR contract N00014-92-J-1280 resulted in 19 papers published in refereed journals and addressed several issues. The main results of these studies will be briefly summarized below. More details can be found in original publications enclosed at the end of this document. Additionally, one PhD thesis resulted solely and one in part from research of this proposal.

The main challenge of this proposal was to apply X-ray standing wave (XSW) technique to study atomic structure of several ordered interfaces. The novel approach adopted in this study was to apply photoelectron detection scheme which allowed us to enhance surface sensitivity of the XSW technique. Additionally, we applied a back reflection configuration to de-emphasize stringent structural requirements put by the technique on the perfection of the substrates. Prior to this proposal XSW technique has been almost exclusively used to study overlayers on Si. The better understood Si and Ge structures has been also studied in our program to test some our approaches. However, most of the research has been performed on more complex III-V and II-VI compound semiconductor surfaces and interfaces. More recently, as a result of the pilot research of this proposal, we were able to study even more complex synthetic material and real minerals. Below we outline some specific areas of research performed under this proposal.

1. Sb and Bi overlayers on GaAs, InP and GaP(110)

The application of XSW to study interfaces and surfaces has been aided by high resolution core level photoemission and Surface Extended X-ray Absorption Fine Structure which were the fields of our expertise prior to this proposal. Our prior experience with these tools allowed the selection of specific interfaces used in the work. Thus we were particularly interested in Sb and Bi overlayers on III-V semiconductors. This emphasis arises because while most metallic overlayers either react or cluster, Sb and Bi forms ordered epitaxial structures. The near ideal morphology of these systems makes them tractable for both theoretical calculations and structural studies. In prior studies we found monolayers of Sb (and also Bi) to passivate GaAs(110) and InP(110) surfaces by saturating all surface dangling bond states. Since the unsatisfied Ga dangling bond states are believed to be the source of the clean surface reactivity the Sb termination (in form of the zig-zag chains)

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chemically "passivates" the surface and limits chemical reactions. Also, at least for InP, the Sb covered surface appears to unpin which can be linked to the reduction of the mid-gap states and implies electrical passivation. For GaAs the status is less obvious. However, since we were to move the surface Fermi level towards the flat band condition on both n- and p-type GaAs by annealing we conclude that the Sb/GaAs interface appears to be at most only lightly pinned. Additionally, we found evidence that monolayer of Sb reduces uptake of oxygen by an order of magnitude. This indicates that chemical reactions are indeed slowed down on the Sb covered surfaces. Although these electronic properties of Sb overlayers are of great scientific and applied interest the atomic structure of this 2-dimensional structures was not fully known. Although STM provided a reliable real space information on the in plane structure, the specific models calculated by LaFemina and others could not be selected due to a lack of the vertical distances. In particular the theory predicted several zig-zag chain structures (as seen those seen by the STM) of almost identical energy but large differences in the vertical distances. This key information could be provided provided by the XSW data. As an example, our XSW work on monolayers of Sb on GaAs(110) gave strong support to the epitaxial continued layer structure model and ruled out other models within the zig-zag chain class. Similar results have obtained for Sb and Bi on GaAs, InP and GaP. The details of these studies on systems of varied complexity have been published. In more complex cases we had to apply we apply the tringulation, ie obtain the stucture from studies from several nonequivalent planes ((220), (111) and (400)). This technique is described in detail in the PhD thesis of Alberto Herrera-Gomez. This thesis also describes mathematical approach to the XSW data analysis. In some cases SEXAFS has been also applied for these interfaces to gain an information on bond lengths and coordinations. Our study of Sb/GaP(110) possibly represents the most complex system to which SEXAFS has ever been applied. More information can be found in the original original papers and Herrera's thesis.

2. Studies of clean surface relaxation

Our research has utilized the unique surface sensitivity of the low energy electron yield with which we monitor the modulation of the standing wave field around the Bragg condition. With this we have developed a new method to study relaxations and reconstructions of clean surfaces. We have applied this method to study relaxation of the InP(110)1x1 surface. The general nature of this relaxation was understood, hence it served as a test bed for a new technique. Despite this general understanding, however, the quantitative displacements of the surface atoms are still questioned, therefore we provided new

quantitative input to compare with the available theoretical calculations. It should be pointed out that, contrary to most other techniques, the atomic specificity of the XSW technique gives a unique capability with which we may determine individual displacements of the In and P surface atoms independently. Our determination for both these displacements are in quantitative agreement with the prior theoretical calculations of Jim Chadi. Additionally, we furthered the understanding of this surface relaxation by combining XSW and SEXAFS. SEXAFS, as a strictly local probe, is unsurpassed in providing extremely accurate near neighbor distances. By applying both SEXAFS and XSW simultaneously, we were able to quantitatively ascertain the bond-length conserving nature of the InP(110) surface relaxation. The experience gained from this system was used in studies of the CdTe surface relaxation. In this work performed in collaboration with John Klepeis (LLNL) and other theorists a combination of XSW measurements and full-potential linear muffin-tin orbital (FP-LMTO) first-principles total energy calculations have determined the surface relaxation of the clean CdTe (110) surface. These two methodologies directly determine the local atomic geometry and therefore provide a model-independent means of verifying the results obtained indirectly from elastic low-energy electron diffraction (ELEED) studies. By comparing our results for this strongly ionic material (Phillips ionicity $f = 0.72$) with the results of numerous earlier studies of less ionic III-V compounds, we are able to assess the influence of ionicity on the degree of relaxation for the cleavage faces of zinc-blende semiconductors. Our measurements and calculations indicate that, contrary to a previous theoretical study but in agreement with ELEED, the relaxation is approximately independent of the semiconductor ionicity. Our model-independent measurements yield a vertical buckling $\Delta_{1,\perp} = 0.120 \pm 0.023$ (in units of the lattice constant; $a = 6.482 \text{ \AA}$) which agrees well with our calculated buckling of 0.114.

3. Monolayers on Si. Influence on overlayers on surface relaxation

With electron detection the XSW technique can be used to study the surface relaxation/reconstruction after the deposition of monolayers of foreign atoms. Since this information eludes other techniques the XSW data provides a unique opportunity to this field of research. For example, one of the key questions in surface science is: does surface reconstruction really matter for interfaces? This question has been addressed for InP(110)1x1-Sb and for Si(111)7x7 covered with 1/3 ML of In. We found that in both cases the initial relaxation or reconstruction is relieved by the overlayer, i. e. the near surface substrate atoms revert to the ideal bulk terminated positions. Although this is perhaps not unexpected for InP for which the relaxation is in the form of a rigid rotation,

the case of the In/Si(111) interface is more instructive because of the complexity of the initial 7x7 surface reconstruction. Additionally, the T₄ bonding geometry, which is found to occur for this particular interface, but more notably, forms a very common building block found in other surfaces and interfaces has been intensively modeled by theorists. The theory suggests that the stability of the T₄ site (in which the second layer Si atom lies just underneath the In) relative to another trifold coordinated site, denoted H₃, is due to a large relaxation of the substrate surface atoms. This relaxation consists of a vertical shift in the second and third layer Si atoms under In and a horizontal contraction of the first layer Si towards the adatom. Our results severely contradict this calculation. We find that the substrate atoms are in ideal (unrelaxed) positions and provide a for the first time a fully quantitative picture of the overlayer structure.

Summary.

Our research has shown that the combination of the XSW and SEXAFS techniques can be particularly powerful in studies of overlayer geometries and clean surface relaxations. Although SEXAFS provides bond-lengths with great accuracy, the coordination numbers are often less reliable. This hampers structural determinations of complex systems; such as metal-semiconductor interfaces which we study. We have shown that, even in these difficult cases the combined information is sufficient to fully determine the overlayer and substrate geometry. The combined XSW/SEXAFS studies have been performed for metal overlayers (Sb, Bi, In, Ag) on Si(111), Ge(111) and III-V substrates. These studies ascertain formation of complicated trimers or zig-zag chains for Sb and Bi on all the substrates we have studied.

Although SEXAFS is of great value in structural determinations, the standing wave technique is fully capable of determining the overlayer geometries. This is achieved by the use of several reflection planes and three-dimensional triangulation of the atomic positions. We have applied this method in the studies of Bi and Sb overlayers on GaAs, InP and GaP and on several overlayers on Si and Ge. Specifically the 220, 111, 11-1, and 200 diffraction planes were used to study the overlayer structure, including the issues of overlayer buckling and structural disorder. When the XSW project was initiated, the emphasis was placed on the determination of the perpendicular distances. This was done under the assumption that this information would supplement the in plane results from STM. However, we find that while STM is of great value for qualitative determinations, it does not provide coordinates of the overlayer atoms. In addition the in plane distances

cannot be extracted from LEED data. Only XSW can provide the in and out of plane information in a model independent manner and with unprecedented accuracy.

In brief, we have successfully applied the XSW technique to the quantitative study of surface and interface structure. We have developed the XSW technique to be a complete tool for most, and not only selected, interfaces. The application of XSW to other problems which go beyond surface science have also been realized and are now being explored.

Publication List and PhD thesis performed under ONR contract N00014-92-J-1280

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X-ray Standing Wave Study of the Bi/GaAs and Bi/GaP Intefaces by Alberto Herrera-Gomez, Stanford University April 1994.